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INVESTIGATION OF COLD COLORED SMOKE PRODUCTION

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INVESTIGATION OF COLD COLORED SMOKE PRODUCTION

by

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ABSTRACT

Different methods for producing large colored smoke clouds for use as spotting charges are evaluated. The problem of the disappearance, or "bleaching", of the orange color from vanadium oxytrichloride ($VOC\ell_3$) clouds during times of high relative humidity is considered. It is postulated that this is caused by the absorption of large quantities of atmospheric moisture by the smoke. A model has been developed to study the process. This model makes the key predictions concerning the absorption of very large amounts of atmospheric moisture by $VOC\ell_3$-type smokes above a relative humidity of 80% and the very small importance of temperature as a parameter. These predictions are, in general, corroborated very well by experiment. Possible solutions to this color bleaching problem are discussed, including one that calls for the synthesis of hydrolyzable vanadium compounds with nonhygroscopic leaving groups.

RÉSUMÉ

On a évalué différentes méthodes pour produire un large volume de fumée de couleur qui est utilisé comme repère. On traite du problème de décoloration de la fumée orange produite par l'oxytrichlorure de vanadium ($VOC\ell_3$) dans des conditions d'humidité de l'air ambiant qui pourraient en être la cause. Un modèle expérimental a été développé dans le but d'étudier le processus. Ce modèle prédit qu'une grande quantité d'humidité atmosphérique est absorbée par la fumée de type $VOC\ell_3$ lorsque l'humidité relative est au-dessus de 80% et considère la température comme un paramètre peu important. Les observations expérimentales corroborent généralement ces prédictions. Des solutions possibles au problème de décoloration sont discutées dont une qui fait appel à la synthèse de composés de vanadium hydrolysés avec des groupes non hygroscopiques.

TABLE OF CONTENTS

ABSTRACT/RÉSUMÉ i

NOMENCLATURE. v

1.0 INTRODUCTION 1

2.0 CRITERIA FOR SMOKE-PRODUCING CHEMICALS USED IN COLD SPOTTING CHARGES 2

2.1 Passive Substances 2
2.2 Active Substances. 3

3.0 COMPOSITION OF SMOKE AND THE GENERAL THEORY OF NUCLEATION . . 5

4.0 DEVELOPMENT OF MODEL 8

4.1 Chemical Aspects 8
4.2 Thermodynamic Aspects 9
4.3 The General Model 12
4.4 Predictions Using the Model 15

5.0 CRITERION AND EXPERIMENTS PERFORMED TO IMPROVE COLOR STABILITY OF HYGROSCOPIC COLORED SMOKES 23

5.1 Criterion 23
5.2 Experiments: Removal of HCl by Chemical Combination . . 24
5.3 Incorporation of Additional Pigment 24
5.4 Preparation of Active Cold Colored Smoke Chemicals with Nonhygroscopic Leaving Groups 26
5.5 Iodine Smokes 28

6.0 CONCLUSIONS AND PLANS FOR FUTURE WORK 30

7.0 ACKNOWLEDGEMENTS 31

8.0 REFERENCES 32

FIGURES 1 to 7

TABLES I to III

APPENDIX A - Properties of Hydrogen Chloride-Water Solutions and Pure Water 33

APPENDIX B - Application of the Hygroscopic Smoke Model . . 35

APPENDIX C - Dissemination Techniques 37

NOMENCLATURE

A,B,C,D,E,F	Usually used as subscripts to indicate a corresponding substance
ΔG	Change in Gibbs free energy for a substance or mixture
M_i	Molecular weight of substance i
N_i	Number of moles of substance i
P_i	Partial pressure of substance i in the atmosphere
P_i^{vap}	Vapor pressure of substance i above pure i
P_i^{sol}	Partial pressure of substance i above a solution containing i
R	Universal Gas Constant
%RH	Percent relative humidity
T	Absolute temperature
V	Total volume of all smoke components, including absorbed atmospheric H_2O
V_i	Volume of solution of i in equilibrium with atmospheric H_2O partial pressure
$V_i^\bullet$	Volume of pure i
W	Total weight of all smoke components, including absorbed atmospheric H_2O
W_i	Weight of solution of i in equilibrium with atmospheric H_2O partial pressure
$W_i^\bullet$	Weight of pure i
c,d,e,f	Stoichiometric coefficients of corresponding substances
r	Radius of droplet (spherical)
x_i	Mass fraction of substance i in a solution of i and solvent
ρ_i	Density of solution of i
$\rho_i^\bullet$	Density (mass/unit volume) of pure i
σ	Interfacial surface tension

1.0 INTRODUCTION

The main objective of this project is to develop a non-fading colored cold smoke composition for use in a signal cartridge for practice bombs. This project was initially undertaken to search for a substance which would produce brightly colored smoke having better color stability in high relative humidity than the currently used vanadium oxytrichloride ($VOC\ell_3$). The primary constraint is that the substance must not require any form of heat to produce the smoke; hence the term "cold smoke". Furthermore, the substance is to be contained within a vial having a maximum volume of about 60 cm^3.

The principal use of the colored cold smoke charge is to mark the point of impact of practice bombs used by the Canadian Forces (CF). Upon impact, the substance is ejected in an atomized form out of the back of the bomb by a bursting charge (black powder is currently being used; see Ref. 1). In summertime, white smoke produced by titanium tetrachloride ($TiC\ell_4$) is satisfactory; however, colored smoke is required during winter because of the white snow background.

Severe constraints placed upon the performance of such cold-smoke agents limits the choice of substances to a very small number. Ideally, what is required is a large, optically dense, brightly colored smoke cloud which is persistent and stable, in terms of both color and volume, under any environmental conditions. Since its purpose is to mark the point of impact of a practice bomb for an aerial observer, the cloud must attain its full volume and color quickly; on the order of 1 or 2 s after bomb impact. Since the charge must not be a fire hazard, no pyrotechnic devices may be used to produce the smoke. The substance must be efficient in producing smoke since its allotted volume is only about 60 cm^3. In addition, there are the usual constraints with regard to reasonable cost, toxicity, availability, and stability under the full range of environmental temperatures. A further obstacle to evaluating different substances or mixtures is the fact that it is

difficult to compare them on any quantitative numerical basis. One is forced to use the human eye to make subjective judgements concerning the quality and "visibility" of a smoke cloud.

This report is divided into two main parts. The first one deals with the development of a model that predicts the effects of environmental conditions (mainly temperature and relative humidity) upon the swelling and color instability of the hygroscopic smokes. The second part gives the results of experiments with different compositions and substances to see which produced the most suitable colored smokes. This work was carried out at DREV between August 1982 and September 1983 under PCN 21B02, Conventional Pyrotechnics.

2.0 CRITERIA FOR SMOKE-PRODUCING CHEMICALS USED IN COLD SPOTTING CHARGES

The basic requirement is for the substance to generate acceptable quantities of aerosol-sized particles upon being disseminated in air without the aid of heat that would be a fire hazard. There are two broad categories into which these aerosol-generating substances may be classed, based mainly upon the presence or absence of a vigorous reaction with water. These two categories have been termed by this author as "active" and "passive". The passive category chemicals are essentially inert to the environment and must be turned into an aerosol by the disseminating agent, usually a high-explosive charge. The active class chemicals are vigorously hydrolyzed by atmospheric water and rely upon this mechanism to disseminate the aerosol.

2.1 Passive Substances

The passive category substances are usually dyes, in a finely powdered form of a type that is similar, if not identical, to the vaporizable dyes used to generate colored smokes from a pyrotechnic device. The high-explosive charge essentially creates a dust cloud of

the dye without the fire hazard of pyrotechnic vaporization. Because of the rather poor smoke clouds produced by high-explosive dissemination of the passive category agents, they, with one exception, have not been considered as candidates for colored cold spotting charges. The one exception noted is elemental iodine (I_2) for which high-explosive (C4 plastic explosive) dissemination has been attempted. Violet clouds of iodine vapor have been produced by this method with good color saturation and apparently excellent stability. Unfortunately violet is not considered a satisfactory color for a spotting charge due to its poor visibility against dark backgrounds such as foliage. The iodine experiments are considered in more detail later in this report. It must be added that iodine, bromine (Br_2), and nitrogen dioxide (NO_2), the last two of which are disseminated like active class chemicals, are in a special class since they produce a highly colored, but nonetheless transparent, vapor as opposed to a cloud of aerosol particles.

2.2 Active Substances

The active category substances generally fume and emit aerosol particles simply upon exposure to the atmosphere and therefore do not require high-energy dissemination techniques. Discharging the active liquid out the rear of the practice bomb by using a small quantity of black powder produces the desired dissemination effect. From a chemical point of view, most of these active substances are halides or oxyhalides of the transition metals, metalloids, and several nonmetals. Most, especially the metal compounds, are in their highest oxidation states. The chlorides are almost always used chiefly because they are the cheapest. Table I lists most of them as well as some of their physical properties. More detailed properties can be found in any suitable reference book (Ref. 2).

It may be noted that of all of these compounds, only two, $VOCl_3$ and CrO_2Cl_2, produce colored smoke, while the rest produce white smoke. The number of active agents for producing colored smoke is limited

TABLE I

Active smoke-producing chemicals

Substance	Formula	Melting Point (°C)	Boiling Point (°C)	Density (g/cm^3)
Titanium Tetrachloride	$TiCl_4$	-24.1	136.4	1.726
Silicon Tetrachloride	$SiCl_4$	-70	57.6	1.483
Tin Tetrachloride	$SnCl_4$	-33	114.1	2.226
Phosphorus Trichloride	PCl_3	-112	75.5	1.574
Phosphorus Oxytrichloride	$POCl_3$	1.25	105.8	1.645
*Chromyl Chloride	CrO_2Cl_2	-96.5	117	1.911
*Vanadium Oxytrichloride	$VOCl_3$	-79.5	126.7	1.829
Chlorosulfonic Acid	$ClSO_3H$	-80	158	1.766
Thionyl Chloride	$SOCl_2$	-105	78.8	1.655
Sulfur Trioxide (γ - Form)	SO_3	16.8	44.8	1.922

*Produce colored smoke. The rest of the substances produce white smoke.

because of the requirement for at least one of the hydrolysis products to be highly colored. In trying to develop a colored active agent that would not fade in high relative humidity, it became obvious that, first, more would have to be known about the fading mechanism and, second, either a mixture or a compound of a new class would have to be employed to meet this goal. It is with this in mind that the next section introduces some of the theory behind the aerosol formation.

3.0 COMPOSITION OF SMOKE AND THE GENERAL THEORY OF NUCLEATION

It is common knowledge that smoke consists of an aerosol of tiny particles suspended in air. These particles may be either solids or liquid droplets. In either case, they are visible in bulk because they affect the passage of light through the smoke. In general, their main effects are light scattering and uniform or selective absorption of certain wavelengths.

There are many mechanical methods by which small particles may be introduced into the air. However, usually to be small enough to qualify as smoke or mist, the dissemination has to be by chemical reaction and/or by a physical condensation process. Both processes are involved in the production of cold smokes using the active class of chemicals. In general, only condensation is involved when the passive category is used. However, since condensation is the most important and interesting mechanism by which smokes and/or aerosols form, it will be examined in detail.

Condensation is purely a physical process, and as the name implies, it involves a phase change whereby a vapor changes to a liquid or solid. Although in some cases the solid may be formed directly, a liquid phase is usually intermediate. There are four distinct processes by which nucleation, or the start of condensation, may occur. As stated by Hamill et al. in Ref. 3, they are:

1. Homogeneous - homomolecular
2. Homogeneous - heteromolecular
3. Heterogeneous - homomolecular
4. Heterogeneous - heteromolecular.

The first type of nucleation, which is the simplest, occurs when a single substance, in vapor form, condenses in completely clean air, i.e. air with no foreign nongaseous particles. An example of this is the condensation of water vapor in ideally clean air. The second type again requires ideally clean air; however, in this case more than one substance condenses from the vapor phase at the same time. The condensed solution has a lower vapor pressure, or volatility, than the sum of the vapor pressures of the pure substances. The condensation of the mixture occurs under conditions which would not cause either of the two pure substances to condense. An example of this would be the formation of sulfuric acid-water (H_2SO_4(aq)) mist when ideally clean air containing sulfuric acid vapor is mixed with similar air containing water vapor. Here, the partial pressure of H_2O in the H_2SO_4(aq) is less than the vapor pressure due to pure water. Similarly, the partial pressure of H_2SO_4 in the H_2SO_4(aq) solution is less than the vapor pressure of pure H_2SO_4.

The last two condensation processes are similar to the first two, except that there are foreign nuclei present in the air upon which nucleation may take place. The heterogeneous-homomolecular process involves the condensation of a pure vapor, such as water vapor, onto particles (usually solid) already present in the atmosphere. Similarly, heterogeneous-heteromolecular nucleation occurs when more than one substance condenses onto a foreign particle.

The homomolecular nucleation processes apply, for the most part, to the chemicals in the passive category. In the case of a standard pyrotechnic colored smoke grenade or generator, the heat from the pyrotechnic composition vaporizes a dye. This dye vapor, once it has

escaped into the atmosphere, cools and condenses to form tiny particles consisting of pure dye. Hence, the process is homomolecular. However, many solid particles are generated by the burning pyrotechnic composition, in addition to those normally present in the air. Because it is thermodynamically much more favorable for the dye vapor to condense out on the particles present, the heterogeneous nucleation process would be by far dominant. For excellent discussions of nucleation, focusing primarily upon the homogeneous-heteromolecular process, see Refs. 4, 5, 6 and 7.

Previous authors (see Refs. 1, 8, 9) have stated they believed the loss of color in the cloud at high relative humidities was due to the pigment particles being coated by a colorless solution of aqueous HCℓ. The fact that coating occurs is supported by nucleation theory since the Gibbs free energy barrier is lower for heterogeneous than for homogeneous nucleation (see Ref. 10). Additionally, it is clear that a beam of light that encounters a colorless acid-water coating will have part of itself reflected before it ever strikes the orange V_2O_5 center. Therefore, at least some of the light will remain white as it passes through the aerosol cloud. As the acid-water envelope grows around the orange central V_2O_5 particle, the surface area of the envelope becomes very large compared with the surface area of the central V_2O_5 particle. When this happens, the enveloped particle begins to scatter light as though the orange V_2O_5 center did not exist. Since an HCℓ-water fog is white, the cloud turns white. As will be seen later, calculations show that the volumes of water absorbed into the HCℓ-water solution become large at high relative humidities; thus the coating of the orange V_2O_5 by thick layers of a colorless solution is likely. The relationship of envelope thickness to degree of bleaching is the last step, and at least a quasi-linear direct relationship is derivable if some simplifying assumptions are made.

It would be ideal if a model could be set up that would predict the environmental conditions under which such thick films would form around an aerosol pigment particle, as well as their rate of formation. Unfortunately, the formulation of such a model is difficult at this time because of its complexity and because certain data, such as an accurate estimate of the size of the V_2O_5 particles, are not known. Nevertheless, it is possible to set up a much simpler model that proves to yield almost as much information as the ideal one.

4.0 DEVELOPMENT OF MODEL

4.1 Chemical Aspects

In order to be able to apply the theory previously discussed to formulate a practical model of hygroscopic smoke behavior, it is helpful to first take a specific example. The only substance currently used by the CF for the production of colored smoke for cold spotting charges is the compound vanadium oxytrichloride ($VOC\ell_3$). At ambient temperatures this compound is a liquid with physical properties as given in Table I. It is in the active class of chemicals and therefore is rapidly hydrolyzed by water vapor according to the reaction:

$$2VOC\ell_3(\ell) + 3H_2O(g) \rightarrow V_2O_5(s) + 6HC\ell(g) \qquad [1]$$

In reality the reaction is more complicated than this and various intermediates may be formed if the water is limited. In addition, the V_2O_5 is most probably hydrated and some lower oxides may form. Nevertheless, this is the main reaction and may be considered the only one for the purposes of modelling.

We note that the V_2O_5 produced is a bright orange solid and is the pigment that gives the $VOC\ell_3$ smoke its orange color. In addition, we see that the small V_2O_5 particles would act as nuclei for the con-

densation of HCℓ-H_2O solution by the heterogeneous-heteromolecular process.

4.2 Thermodynamic Aspects

For a heteromolecular condensation process limited to two substances, the change in Gibbs free energy in going from vapor to liquid, assuming ideal gas, may be expressed as:

$$\Delta G\ (N_A, N_B) = -N_A RT\ \ell n\ (\frac{P_A}{P_A^{sol}}) - N_B RT\ \ell n\ (\frac{P_B}{P_B^{sol}}) + 4\pi r^2 \sigma \qquad [2]$$

where A = solvent (H_2O),
B = acid or solute,
N_i = the number of moles of i,
P_i = the partial pressure of pure i in the gas phase,
P_i^{sol} = the partial pressure of i in a solution of A and B,
ΔG = the change in Gibbs free energy,
R = the Universal Gas Constant,
T = absolute temperature,
r = droplet radius, and
σ = the surface tension of the solution.

According to experiments performed by Gillespie et al. (see Ref. 10), common acid mists such as those of HCℓ and H_2SO_4 have particle radii of 1 or 2 μm. The smallest is H_2SO_4 mist produced from SO_3 with radii of about 0.2 μm. For these relatively large radii the surface free energy term, or "Kelvin Effect", may be neglected (see Refs. 10, 11).

The fact that the Kelvin Effect (third term, right-hand side of eq. 2) becomes negligible for large r's may not seem obvious at first. However, the N_i's in the first and second right-hand terms are

actually proportional to r^3, making the contribution of the r^2 in the Kelvin Effect term of small importance by comparison. The relation is:

$$N_i(r) = \frac{4\pi r^3 x_i \rho}{3M_i} \qquad [3]$$

So that eq. 2 could be rewritten as:

$$\Delta G(r) = \frac{-4\pi r^3 x_A \rho\ RT}{3M_A} \ln\left(\frac{P_A}{P_{A\,sol}}\right) - \frac{4\pi r^3 x_B \rho\ RT}{3M_B} \ln\left(\frac{P_B}{P_{B\,sol}}\right) + 4\pi r^2 \sigma \qquad [4]$$

where x_i = the mass fraction of solute i in a solution of solvent and i,

ρ = density of solution, and

M_i = molecular weight of i.

Going back to the original form of eq. 2 and deleting the "Kelvin Effect" term:

$$\Delta G = -N_A RT \ln\left(\frac{P_A}{P_{A\,sol}}\right) - N_B RT \ln\left(\frac{P_B}{P_{B\,sol}}\right) \qquad [5]$$

Nucleation will occur if $\Delta G<0$. The limiting condition, equilibrium, occurs when $\Delta G=0$:

$$N_A \ln\left(\frac{P_A}{P_{A\,sol}}\right) + N_B \ln\left(\frac{P_B}{P_{B\,sol}}\right) = 0. \qquad [6]$$

The assumption is now made that the atmospheric partial pressure of acid (B) is equal to the partial pressure of acid above the acid-water droplets. This condition is completely true only after total

equilibrium is achieved, but, except for very small acid concentrations, a good approximation is attained after a short period of time under normal conditions. Therefore, we put in the condition that $P_B = P_B^{sol}$:

$$N_A \ln \left(\frac{P_A}{P_A^{sol}}\right) = 0. \qquad [7]$$

Since $N_A \neq 0$, the condition for equilibrium is:

$$P_A = P_A^{sol}. \qquad [8]$$

Equation 8 is the relationship that limits the amount of atmospheric moisture absorbed by a hygroscopic smoke. Next, we relate P_A to environmental conditions. In general, we may write:

$$P_A = P_A^{vap}(T) \frac{\%RH}{100\%} \qquad [9]$$

where P_A^{vap} = the vapor pressure of pure A at a temperature T, and

%RH = the percent relative humidity.

Combining eqs. 8 and 9, we obtain eq. 10 which shows that it is possible to relate %RH and T to x, the mass fraction of acid in water solution in the cloud:

$$P_A^{sol}(x,T) = P_A^{vap}(T) \frac{\%RH}{100\%} \qquad [10]$$

Equation A-I in Appendix A shows how x may then be related to P_A^{sol} (where A = H_2O) and T.

4.3 The General Model

In the previous section the thermodynamic basis for a hygroscopic smoke model was developed. This section will deal with producing relations to connect the thermodynamic constraints to the stoichiometric behavior of an active smoke chemical. By doing this, a general and practical model is set up that is capable, for a given substance, of predicting the amount of atmospheric moisture absorbed as a function of temperature and relative humidity.

Equation 10 shows that for a given temperature, x (the acid concentration in solution) may be found for any relative humidity. What is required now is a mass balance to relate this x to quantities such as final smoke weight and volume. To facilitate this, first we write a general hydrolysis reaction that can be applied to almost all of the active smoke chemicals:

$$cC + dH_2O\ (g) \rightarrow eE + fF \qquad [11]$$

where c, d, e, f are the stoichiometric coefficients,
C is the active smoke chemical, and
E, F are the products.

After a mass balance and some algebraic manipulation, we obtain a generalized relation:

$$\frac{W}{W_C^\circ} = \frac{1}{cM_C}\left[\frac{eM_E}{x_E} + \frac{fM_F}{x_F}\right] \qquad [12]$$

where W = total weight of all smoke components, including absorbed atmospheric H_2O,
W_i° = weight of pure i, and
x_i = the mass fraction of solute i in a solution of H_2O solvent and i.

If, as in most cases, one of the products is insoluble, then its x_i is unity. In the case of colored smokes, it is also useful to have the following relation:

$$\frac{W_E}{W_F} = \frac{eM_E\ x_F}{fM_F\ x_E} \qquad [13]$$

where W_i = weight of solution of i in equilibrium with atmospheric water vapor.

Volumetric ratios would be even more useful since volume is more directly related to the visibility of a smoke. On a volumetric basis, eqs. 12 and 13 take the form:

$$\frac{V}{V_C^\circ} = \frac{\rho_C^\circ}{cM_C}\left[\frac{eM_E}{\rho_E x_E} + \frac{fM_F}{\rho_F x_F}\right], \text{ and} \qquad [14]$$

$$\frac{V_F}{V_E} = \frac{fM_F\ x_E \rho_E}{eM_E\ x_F \rho_F} \qquad [15]$$

where V = total volume of all smoke components, including absorbed atmospheric H_2O,

V_i° = volume of pure i,

V_i = volume of solution of i in equilibrium with atmospheric H_2O partial pressure,

ρ_i° = density of pure i, and

ρ_i = density of solution of i in H_2O, at concentration x.

See Appendix B for application of the model to $VOC\ell_3$ and $CrO_2C\ell_2$.

One final and important relationship is the one between water uptake and the degree of bleaching. Although, intuitively, such a relationship would seem to be linear, after some discussion it was realized that a quantitative basis for this assumption would have to be made.

Figure 1 represents what is believed to be a typical case of a smoke pigment particle in a high relative humidity environment. The bleaching is caused by the $H_2O/HC\ell$ envelope not allowing photons to strike the pigment center (i.e. due to scattering). The degree to which this envelope is able to capture and scatter photons is assumed directly proportional to its cross-sectional area. The amount of water in the envelope, on the other hand, is directly related to the volume of the envelope, since the $HC\ell/H_2O$ solution is very dilute (usually $<<$ 5%). The central V_2O_5 particles are assumed to take up only an insignificant volume.

From the previous discussion, we may therefore write:

$$\text{bleaching} \propto \text{cross-sectional area } (\pi r^2) \qquad [16]$$

or

$$\text{bleaching} \propto r^2 \qquad [17]$$

and

$$H_2O \text{ uptake} \propto \text{volume of droplet } (\simeq 4/3\pi r^3) \qquad [18]$$

or

$$H_2O \text{ uptake} \propto r^3. \qquad [19]$$

Therefore, we obtain:

$$\text{bleaching} \propto (H_2O \text{ uptake})^{2/3}. \qquad [20]$$

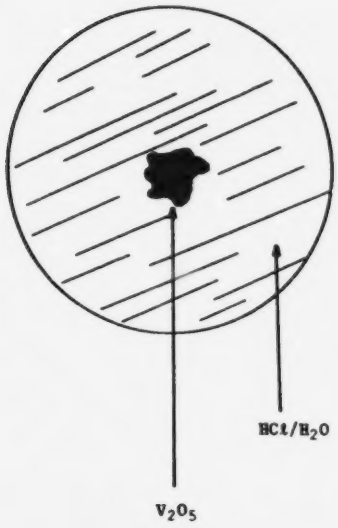


FIGURE 1 - Smoke pigment particle in high relative humidity environment

This simplified picture at least allows the statement that the amount of moisture absorbed from the atmosphere, which is what the model predicts, is roughly directly related to the degree of color loss or bleaching.

4.4 Predictions Using the Model

As mentioned previously, the model is applied to $VOCl_3$ and CrO_2Cl_2 smokes. Figures 2-7 show the results from which several implications may be drawn. First, and most important, one sees from Figs. 2 and 3 that the smokes really begin to take up water beyond a relative humidity of about 80%. Water uptake becomes critical at a relative humidity of about 95%. This agrees well with experimental observations of both this and previous authors (see Refs. 1, 8, 9), if water uptake is taken as being directly related to color bleaching, as discussed in the previous section.

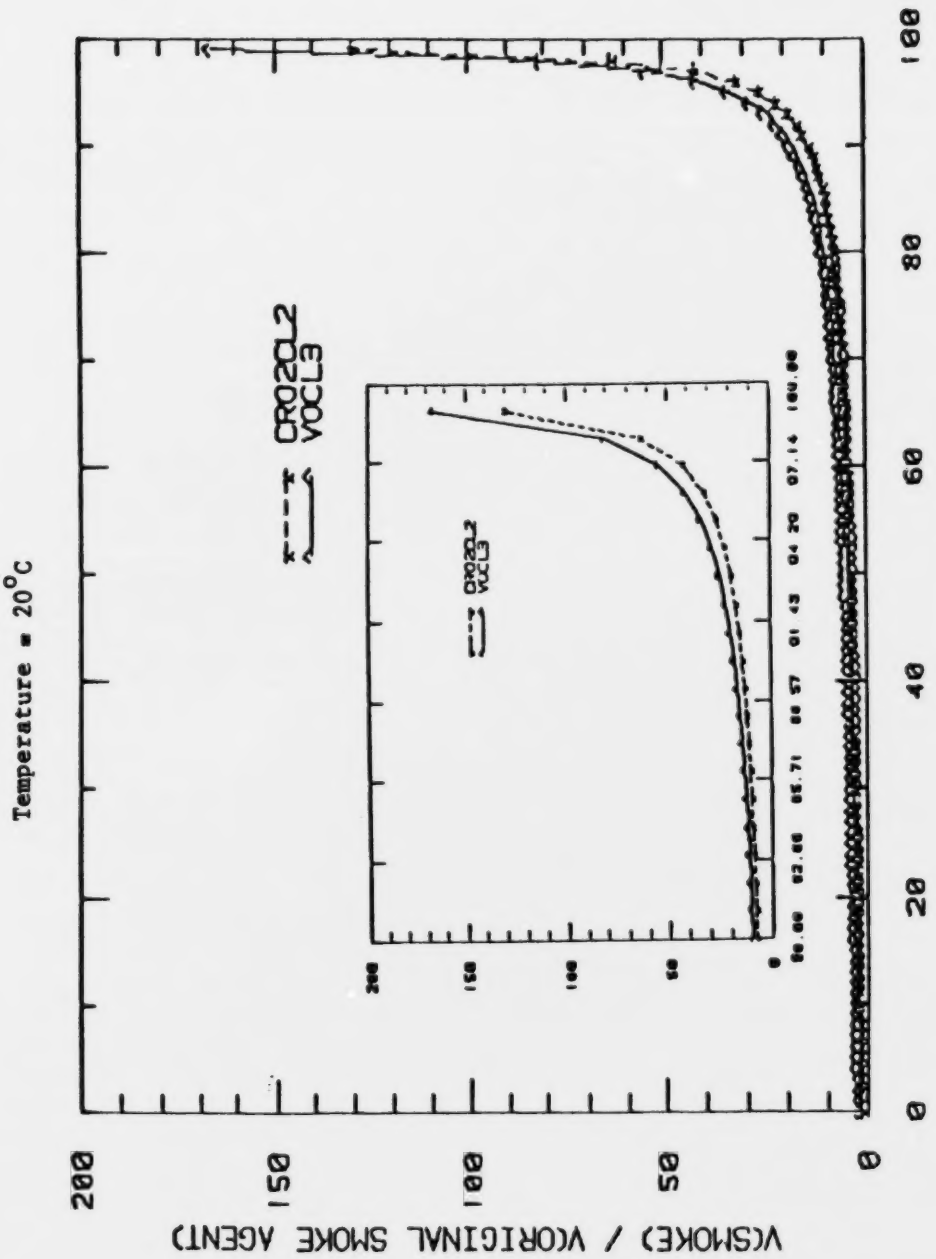


FIGURE 2 - Comparison of $VOCl_3$ and CrO_2Cl_2 smokes

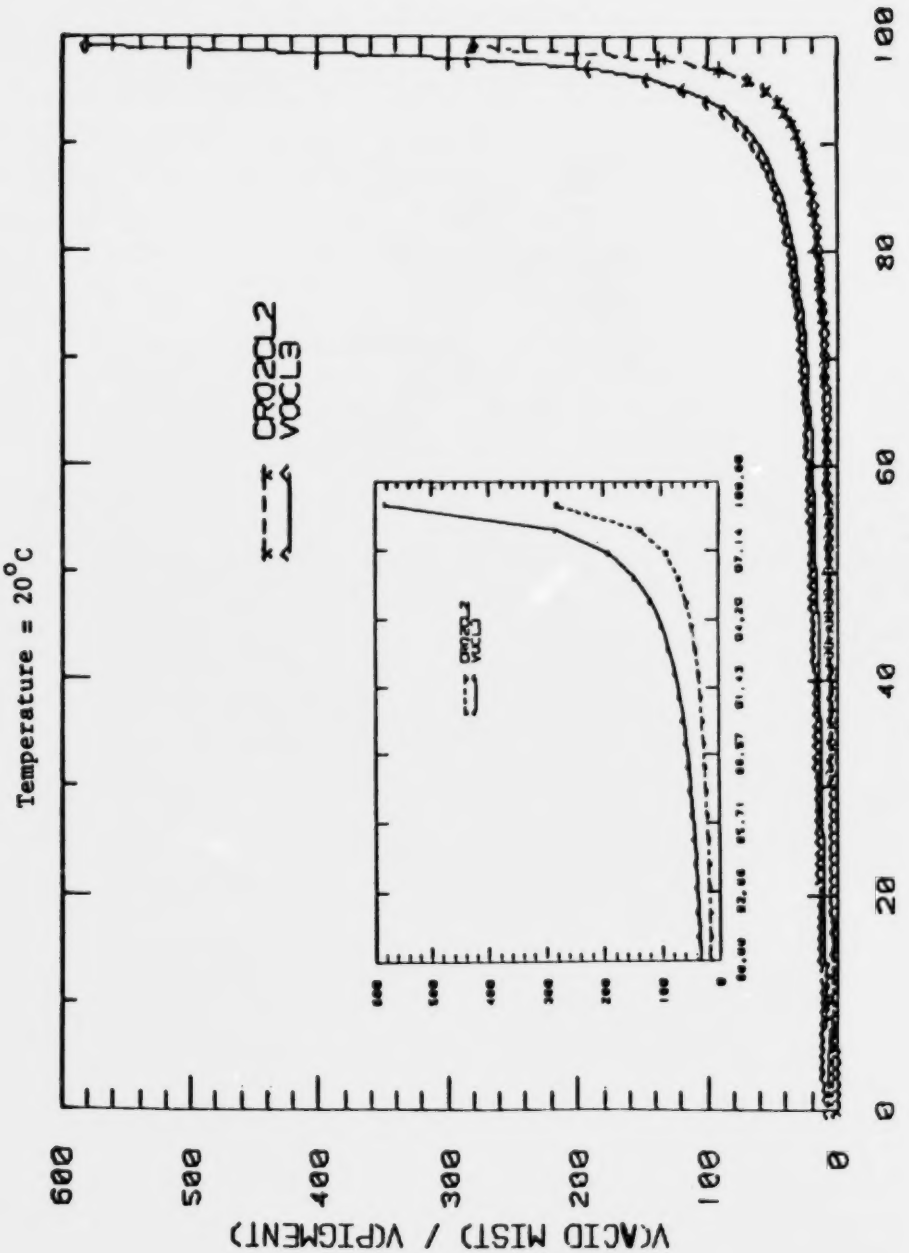


FIGURE 3 - Comparison of $VOCl_3$ and CrO_2Cl_2 smokes

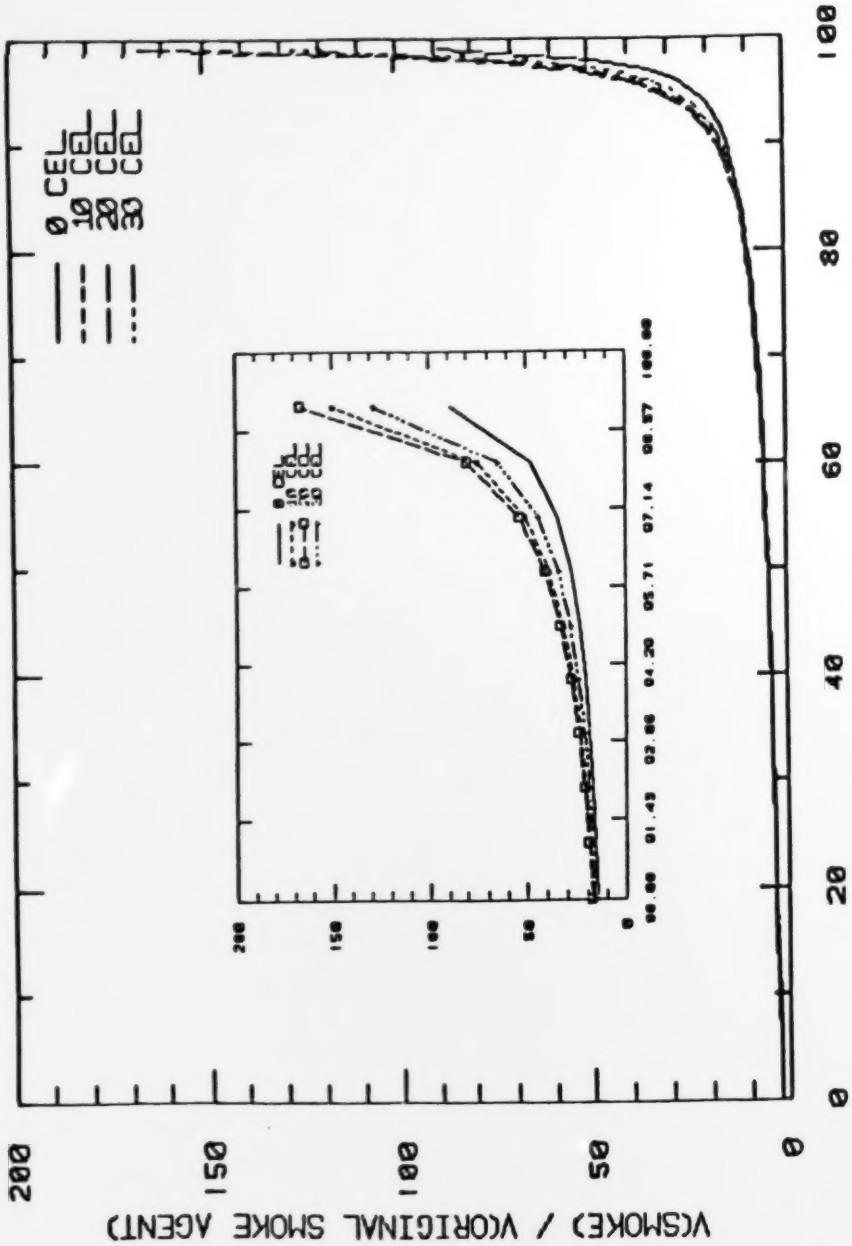


FIGURE 4 - $VOCl_3$ smoke: effect of temperature
V(smoke)/V($VOCl_3$)

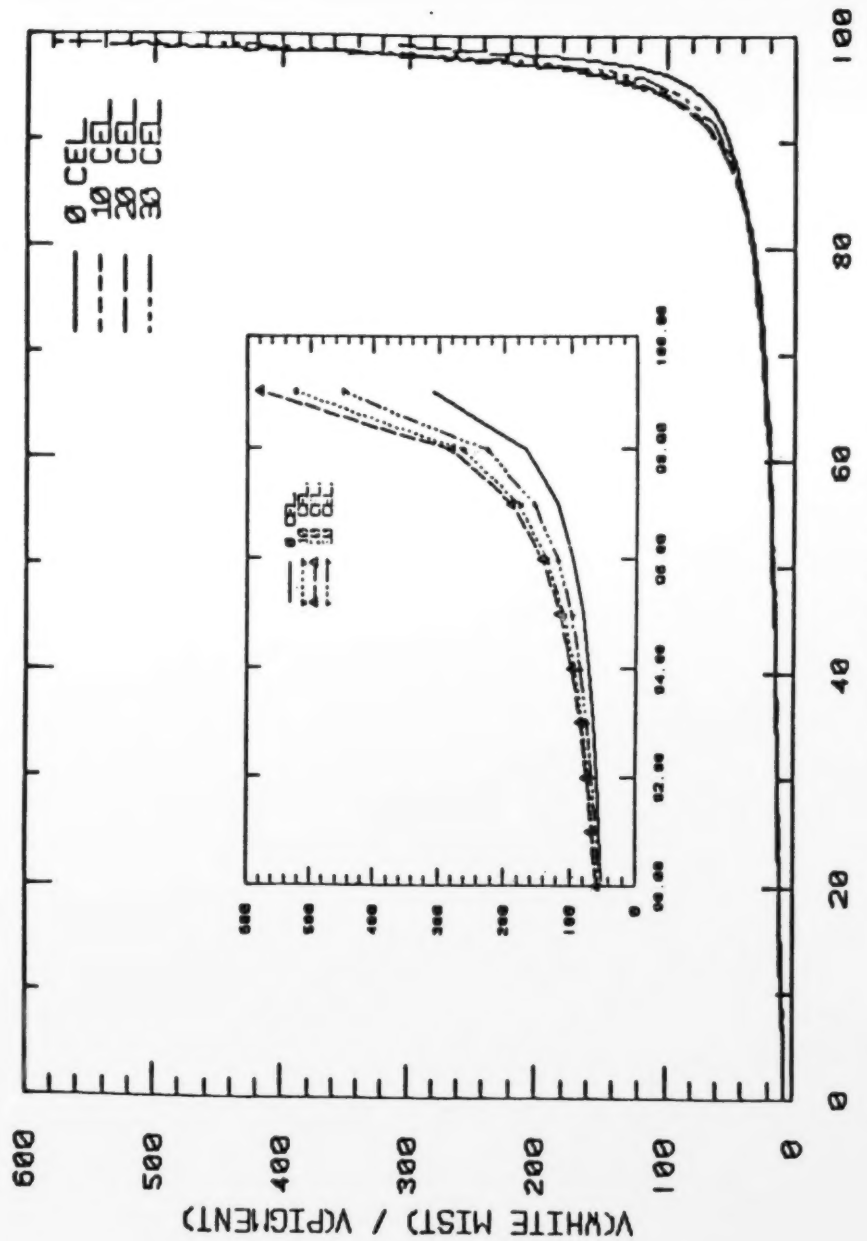


FIGURE 5 - $VOCl_3$ smoke: effect of temperature
V(white HCl acid mist)/V(V_2O_5 pigment)

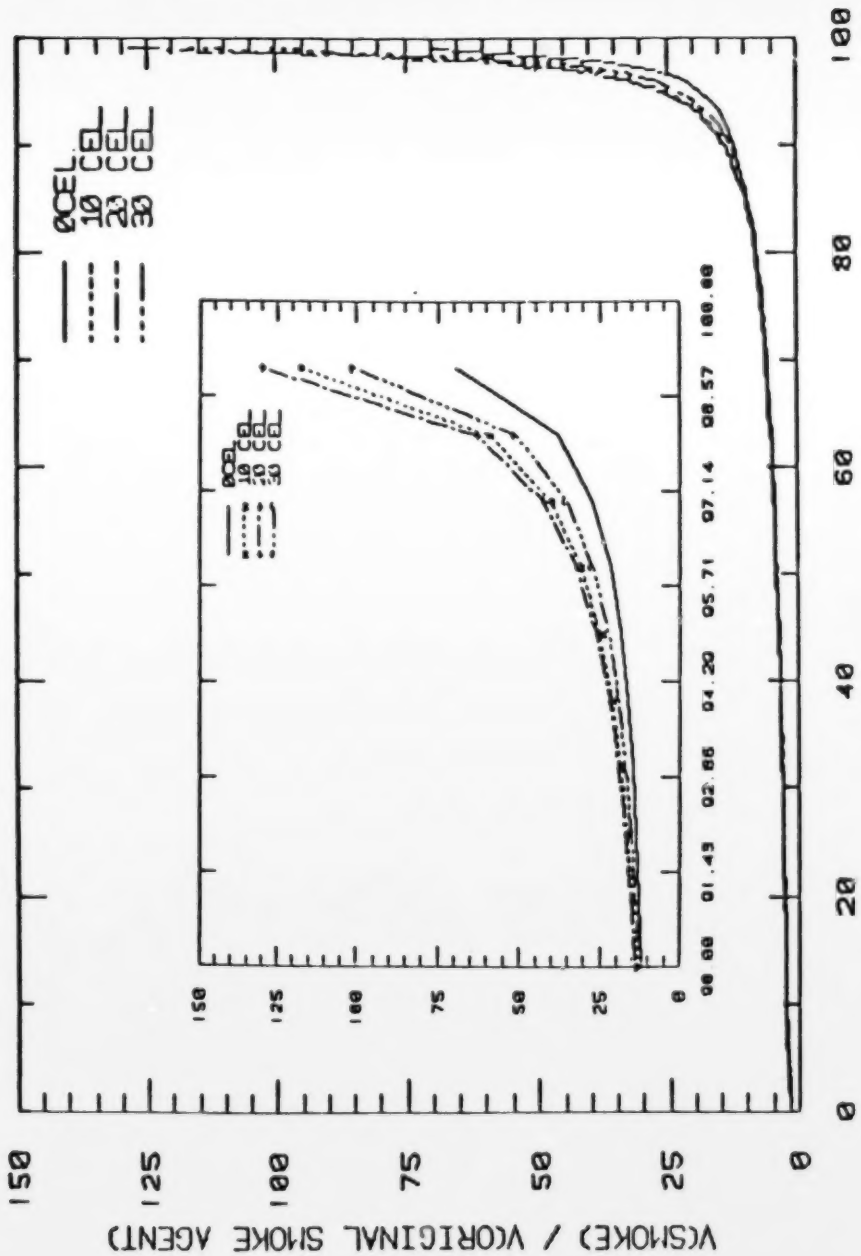


FIGURE 6 - CrO_2Cl_2 smoke: effect of temperature
$V(smoke)/V(CrO_2Cl_2)$

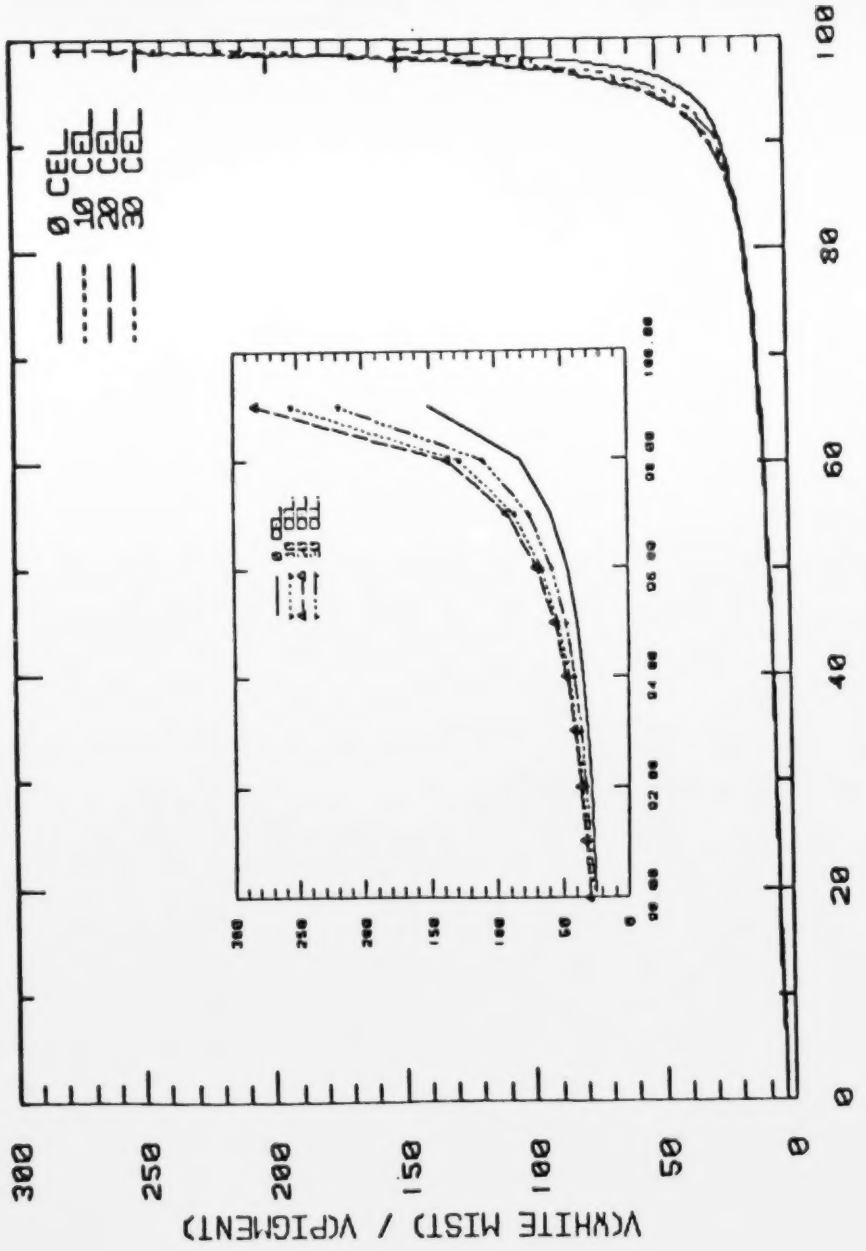


FIGURE 7 - CrO_2Cl_2 smoke: effect of temperature
V(white HCl acid mist)/V(CrO_3 pigment)

A second prediction becomes apparent when one looks at Figs. 4-7. The almost negligible effect of temperature upon the hygroscopic properties of the smokes is mentioned in the report by Tatyrek (see Ref. 8). It is felt the model's temperature effect predictions make it unnecessary to include temperature as a parameter in any further experimental studies of this subject. Finally, Figs. 2 and 3 indicate that CrO_2Cl_2 smoke would tend to be somewhat less hygroscopic than $VOCl_3$ smoke. Indeed, it has been observed experimentally that CrO_2Cl_2 smoke has a higher color stability than $VOCl_3$ smoke at high relative humidity (>90%). Unfortunately, the initial color of the CrO_2Cl_2 smoke (with CrO_3 as pigment) was considerably poorer than that of $VOCl_3$ smoke (with V_2O_5 as pigment). Therefore, any benefit from decreased hygroscopic tendency was negated by the initial poorer color.

All the predictions made by the model seem to fit the actual behavior of the hygroscopic smokes. Although the model is of a static-equilibrium type, it appears quite successful in making several key predictions. Its success hinges upon two main factors. First, virtual equilibrium is achieved quickly (on the order of 1-10 s, depending upon the relative humidity). Second, even though the exact relation between water absorbed and color bleaching may not be precisely known, the curves generated show a sudden rise with relative humidity, making it easy to estimate at what point the cloud will bleach. It is believed that the general form of the model will prove quite useful for simplified comparisons of different hygroscopic smoke agents.

5.0 CRITERION AND EXPERIMENTS PERFORMED TO IMPROVE COLOR STABILITY OF HYGROSCOPIC COLORED SMOKES

5.1 Criterion

Once a rudimentary knowledge of the behavior and reason for color fading of the presently used $VOC\ell_3$ smokes was acquired, basic screening experiments were begun at DREV. The primary aim was to obtain a cold colored smoke with significantly improved color stability with respect to relative humidity.

The model indicates that the main criterion for achieving this goal is to decrease the quantity of HCℓ produced per unit of pigment; ideally down to zero. If there is less HCℓ to absorb atmospheric moisture, there will be less $HC\ell/H_2O$ solution to coat the pigment particles at a given relative humidity. It must be added that what applies to HCℓ in the previous discussion really applies to any hygroscopic gas that is produced along with the pigment. Thus, the HBr produced if $VOBr_3$ were used would be just as much of a problem as HCℓ, as would the HF produced if CrO_2F_2 were used.

Three basic approaches are used to meet the requirement for reduced HCℓ production. The first two have been utilised in the DREV screening experiments, the third will possibly be contracted out to a university. The approaches may be listed as follows:

1. Chemically combine the HCℓ into a hygroscopically inactive form.

2. Attempt to incorporate additional pigment into the active colored smoke agent. This technique may result in simple dissolution or a chemical combination of pigment with the solvent.

3. Prepare active colored cold smoke agents which would have only relatively nonhygroscopic leaving groups.

5.2 Experiments: Removal of HCℓ by Chemical Combination

This approach used chemicals that were known to react with HCℓ. It was hoped they would act as scavengers and combine with the HCℓ to form a relatively nonhygroscopic product. Since all of these compounds vigorously combine with either $VOC\ell_3$ or $CrO_2C\ell_2$, the experiments were performed either by mixing the vapors of the compound and $VOC\ell_3$ or $CrO_2C\ell_2$ under a fume hood, or by using separate glass vials with the mortar dissemination method. Table II lists the results of the various combinations that were tried. As can be seen from this table, none of the smokes obtained showed any improvement in color or color stability over $VOC\ell_3$. These poor results are, in most cases, believed to be caused by a deposition of the hydrochloride salt of the scavenger, which is white, on the V_2O_5 particles. In other cases, there is a REDOX reaction, and the vanadium is reduced from the orange + 5 oxidation state. In any case, from these experiments it is judged that this approach will not produce any desirable results.

5.3 Incorporation of Additional Pigment

This concept was originally attempted by Wall (see Ref. 9) when he added vanadium pentoxide (V_2O_5) powder to $VOC\ell_3$. However, V_2O_5 is virtually insoluble in $VOC\ell_3$ at ambient conditions and thus one would not expect to see a significant improvement in smoke color. His results reflect this. Since CrO_3 is the pigment component of $CrO_2C\ell_2$ colored smoke, it was decided to try to incorporate it into $VOC\ell_3$. It was found that CrO_3 was somewhat soluble in $VOC\ell_3$ at room temperature (~5% by weight). As the CrO_3 is dissolved, the liquid turns from the light yellow-orange color of pure $VOC\ell_3$ to a very deep blood-red color resembling $CrO_2C\ell_2$. Furthermore, a precipitate of what appears to be

TABLE II

Reaction of $VOCl_3$ and CrO_2Cl_2 with HCl absorbing compounds

	Reactants	Conditions	Observations
1)	$VOCl_3$ NH_3	vapors mixed	pale green smoke rapidly turns white
2)	$VOCl_3$ N_2H_4	vapors mixed	very pale green smoke, rapidly turns white violent inflammation if the liquids are mixed
3)	$VOCl_3$ $C_2H_4(NH_2)_2$	simultaneously fired out of mortar in 2 separate glass vials	white smoke
4)	CrO_2Cl_2 NH_3	vapors mixed	white smoke
5)	CrO_2Cl_2 N_2H_4	vapors mixed	white smoke explosion if liquids mix
6)	CrO_2Cl_2 $C_2H_4(NH_2)_2$	vapors mixed	white smoke
7)	$VOCl_3$ $CH_2(NH_2)-CH(NH_2)-CH_3$	vapors mixed	blackish smoke quickly turns white
8)	$VOCl_3$ $NaNH_2$	liquid and solid mixed	inflammation (violent) greenish smoke quickly turns white
9)	$VOCl_3$ $CH_2-CH(O)-CH_3$	vapors mixed	greenish-white smoke

V_2O_5 is deposited overnight. Only this insoluble precipitate remains when the solution is boiled off. It is strongly suspected that a reaction of the type shown in eq. 21 occurs:

$$2VOCl_3 + 3CrO_3 \rightarrow 3CrO_2Cl_2 + V_2O_5\downarrow \qquad [21]$$

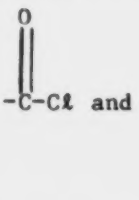
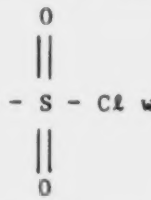
Several tests have been made with saturated CrO_3 in $VOCl_3$ solutions by disseminating them with the mortar method. There appears to be some improvement in initial smoke color at moderately high relative humidities (~80%) and color persistance appears 10-20% longer. Nevertheless, there is no dramatic improvement and the smoke still bleaches quickly. The small improvement is judged not significant enough to warrant the implementation of the CrO_3. Tatyrek (Ref. 8) mentions that CrO_2Cl_2 saturated with CrO_3 gives a smoke of a superior color to that of CrO_2Cl_2 alone, but this has not yet been tried at DREV.

5.4 Preparation of Active Cold Colored Smoke Chemicals with Nonhygroscopic Leaving Groups

This concept would appear to be the natural solution to the problem of smoke bleaching. Originally, it was hoped dyes of the type used in pyrotechnic colored-smoke-generating devices could be chemically modified to form vigorously hydrolyzable active substances. These substances would then combine with atmospheric H_2O to re-release the dye in an aerosol form. The process would be analogous to what already happens with $VOCl_3$ except that:

a) the active dye's leaving groups would not necessarily be hygroscopic; and

b) if the leaving groups were hygroscopic, it would be hoped a highly colored pigment could be chosen that would not be as easily masked as V_2O_5.

It was generally felt that chemically modifying a dye into such an active substance could be difficult. The usual actively hydrolyzable groups such as  and  would be inhibited by the bulkiness of the large dye molecule. Finally, it was suggested that V_2O_5 be kept as the aerosol pigment but that its active precursor, presently $VOC\ell_3$, be changed to a vanadium (V) compound which is still readily hydrolyzed but whose hydrolysis products are nonhygroscopic.

The existence of readily hydrolyzable compounds of the general form

was first noted in the open literature in the book by Sidgwick (see Ref. 12). Sidgwick describes the so-called "vanadic esters", or vanadium (V) alkoxides, where R = C_2H_5, C_3H_7, ... (the methyl ester is apparently not well known). These compounds were investigated in detail by Prandtl and Hess (see Ref. 13). They are described as pale yellow relatively involatile liquids. According to the data of Lachowicz et al. (see Ref. 16), $VO(OC_2H_5)_3$ boils at about 72°C (under 2 mm Hg). It is readily hydrolyzed by water, first to highly colored condensed-acid esters of the type $R_3V_3O_9$ and $R_3V_5O_{14}$, and finally to hydrated V_2O_5 and ROH.

The general preparatory scheme used by the earlier investigators was the alchoholysis of V_2O_5 or NH_4VO_3 (see Ref. 14), as given in eqs. 22 and 23.

$$V_2O_5 + 6ROH \rightarrow 2R_3VO_4 + 3H_2O \qquad [22]$$

$$NH_4VO_3 + 3ROH \rightarrow R_3VO_4 + NH_3 + 2H_2O \qquad [23]$$

However, because of the H_2O formed, these schemes have an efficiency of only several percent. A more satisfactory method, one that has been tried for R = C_2H_5 by this author, is the one described by Bradley et al. (see Ref. 15) and represented by eq. 24:

$$VOCl_3 + 3RONa \xrightarrow{ROH} \begin{matrix} & & OR \\ & & \diagdown \\ O & = & V \\ & & \diagup \\ & & OR \end{matrix} \quad OR + 3NaCl\downarrow \qquad [24]$$

The reaction is vigorous, it goes to completion, and the insoluble NaCl may be filtered off, leaving a solution of R_3VO_4 in ROH. Furthermore, by varying the stoichiometry, compounds of the R_2ClVO_4 and RCl_2VO_4 type may be prepared.

The solution of $(C_2H_5)_3VO_4$ in C_2H_5OH that was obtained does not fume in air under normal conditions, but a yellow smoke is obtained upon intense boiling. It is hoped that future research work will yield more active derivatives which will prove capable of producing the desired V_2O_5 aerosol without excessive water absorption.

5.5 Iodine Smokes

Finally, it was realized that a colored cloud could be produced by disseminating a highly colored vapor into the air. Only three candidates were found suitable for this purpose. They were the halogens bromine (Br_2) and iodine (I_2), and the brown gas, nitrogen dioxide

(NO_2). The standard mortar method (see Appendix C) was found suitable for disseminating the liquid Br_2 and NO_2, however C4 plastic explosive was used with the less volatile I_2 crystals.

The objective of the iodine (I_2) experiment was to produce the largest possible amount of I_2 vapor using a limited amount of I_2 and explosives. The explosion scatters and vaporizes the I_2, forming a purple cloud. C4 explosive was employed and the dissemination was successful.

Six such charges were made; between 20 and 100 g of I_2 was used and the explosive charge consisted of between 10 and 40 g of C4. The C4 was the limiting factor in the amount of I_2 vapor produced and the best clouds were those with the largest amount of C4, virtually irrespective of the I_2 content. In one case, it was the I_2 that was surrounded by the C4, but this change had little effect upon the resulting cloud. The cloud volume and optical density with the 40-g C4 charges were very good, and no color fading was noticed even after 30 s. The relative humidity was about 70%. It is believed that hotter explosion-plasma temperatures, and hence higher I_2 vaporization efficiencies, could be obtained by using additives such as Al powder, or by using other explosives. Nevertheless, further development work using the I_2 smokes has been stopped due to the unacceptable violet color which has a poor visibility against a dark background. See Table III for the charge compositions used.

TABLE III

Compositions of iodine charges

Charge #	I_2 (g)	C4 (g)
1	50	10
2	50	30
3a	20	40
3b	20	40
4	100	10
5	100	40

Note: Charge 3b has I_2 surrounded by C4; all other charges have C4 surrounded by I_2.

6.0 CONCLUSIONS AND PLANS FOR FUTURE WORK

Several important steps have been taken towards reaching the goal of producing a nonfading colored cold spotting charge. The cause of the problem of color bleaching in the currently used $VOC\ell_3$ smoke has been postulated as being due to the absorption of large quantities of H_2O at high relative humidities. This postulate is supported with the aid of a thermodynamic model that predicts absorption of critically large amounts of H_2O by the hygroscopic smoke at relative humidities where bleaching of color can be seen to occur. The model also predicts virtual independence of temperature as a parameter in the color bleaching process. This agrees with experimental evidence. Graphs are produced that predict the behavior of $VOC\ell_3$ and $CrO_2C\ell_2$ smokes at different temperatures and relative humidities. The model is put into a general form so that it may be used to predict the behavior of virtually any hygroscopic smoke agent.

Experimentally, attempts to scavenge the hygroscopic $HC\ell$ out of $VOC\ell_3$ smoke and to incorporate more pigment into $VOC\ell_3$ have shown little promise. Organometallic vanadium (V) esters seem to have the desired properties but have only begun to be explored. Work is presently being considered to prepare various types of esters for study.

In order to better understand the V_2O_5 aerosol, plans are being made to measure the size distribution of $VOC\ell_3$ smoke particles and to use this information in a Monte Carlo photon scattering program to model the effect of such a cloud upon light passage under different relative humidities.

7.0 ACKNOWLEDGEMENTS

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APPENDIX A

Properties of Hydrogen Chloride-Water Solutions and Pure Water

A.1 Partial Pressure of H_2O Vapor over H_2O/HCℓ Solutions

(Source: Chemical Engineers' Handbook (see Ref. 12, Table 3-10).)

The objective is to obtain the mass fraction of HCℓ in HCℓ/H_2O solution as a function of H_2O partial pressure and temperature. The data has been put into functional form with the aid of an 8-term power series. The relation is of the form:

$$x_{HC\ell}\ (P^{sol}_{H_2O}) = \sum_{k=0}^{7} A_k (P^{sol}_{H_2O})^k \qquad [P^{sol}_{H_2O}] = \text{mm Hg} \qquad [A\text{-}1]$$

The series constants, A_k, are given below in Table A-I. The concentration range is $x = 0 \rightarrow 0.42$ (by weight).

TABLE A-I

Power series constants

k	A_k			
	0°C	10°C	20°C	30°C
0	.51667	.51861	.52947	.54634
1	- .43422	- .18691	- .098601	- .055331
2	.50958	.088623	.024017	6.9536×10^{-3}
3	- .43305	- .031064	-4.4104×10^{-3}	-6.8069×10^{-4}
4	.22115	6.5923×10^{-3}	4.9504×10^{-4}	4.2561×10^{-5}
5	- .064975	-8.1498×10^{-4}	-3.2528×10^{-5}	-1.6149×10^{-6}
6	.010028	5.3589×10^{-5}	1.1380×10^{-6}	3.3424×10^{-8}
7	-6.2774×10^{-4}	-1.4552×10^{-6}	-1.6411×10^{-8}	-2.8894×10^{-10}

A.2 Densities of $HC\ell/H_2O$ Solutions

(Source: Ref. 2, Table 3-59)

It was found that the densities of the solutions could be very well represented by linear equations. The concentration range is $x = 0 \rightarrow 0.30$ except at $T = 20°C$, where $x = 0 \rightarrow 0.40$. The fitting was done on an HP 33E calculator which uses a best fit technique. The results are given below in Table A-II. Table A-III gives the vapor pressures of H_2O at various temperatures.

TABLE A-II

Densities of $HC\ell/H_2O$ solutions

T (°C)	$\rho_{HC\ell}(x)$ [g/cm^3]	Number of data points	SR*
0	0.99936 + 0.53818 x	16	0.99997
10	0.99899 + 0.51925 x	16	0.99995
20	0.99763 + 0.50326 x	21	0.99997
30	0.99509 + 0.49296 x	16	0.99996

* SR = Spearman's Rank Correlation Coefficient

TABLE A-III

Vapor pressures of pure H_2O

T (°C)	$P^{vap}_{H_2O}$ [mm Hg]
0	4.581
10	9.203
20	17.53
30	31.81

APPENDIX B

Application of the Hygroscopic Smoke Model

B.1 The $VOC\ell_3$ Case

Equation 1, the hydrolysis reaction for $VOC\ell_3$, is:

$$\underset{(C)}{2\ VOC\ell_3(\ell)} + \underset{(D)}{3\ H_2O(g)} \rightarrow \underset{(E)}{V_2O_5(s)} + \underset{(F)}{6\ HC\ell(g)}$$

Comparing eq. 1 with eq. 11, we have: c=2, d=3, e=1, f=6, M_C=173.32, M_E=181.9, M_F=36.46, ρ_C°=1.829 g/cm^3. Since V_2O_5 is insoluble, x_E=1.0, $V_E = V_E^\circ$ and $\rho_E=\rho_E^\circ$=3.357 g/cm^3. Therefore, from eq. 14 we obtain:

$$\frac{V}{V_C^\circ} = \frac{1.1543}{\rho_F\ x_F} + 0.2859 \qquad [B\text{-}1]$$

From equation 15 we obtain:

$$\frac{V_F}{V_E^\circ} = \frac{4.0373}{\rho_F\ x_F} \qquad [B\text{-}2]$$

where the subscript F refers to HCℓ solutions. For a given temperature and relative humidity, one may obtain x_F from Appendix A which gives the physical properties of $HC\ell/H_2O$ solutions in functional form. Knowing x_F, ρ_F is also easily obtained from Appendix A. In this way graphs may be plotted of the ratios V/V_C° and V_F/V_E° versus relative humidity. Figures 2 and 3 give a comparison of these hygroscopic properties for $VOC\ell_3$ and $CrO_2C\ell_2$ smokes. Figures 4 and 5 give the ratios for $VOC\ell_3$ at various temperatures.

B.2 The CrO_2Cl_2 Case

The hydrolysis of CrO_2Cl_2 is idealized by the following reaction:

$$\underset{(C)}{CrO_2Cl_2(\ell)} + \underset{(D)}{H_2O(g)} \rightarrow \underset{(E)}{CrO_3(s)} + \underset{(F)}{2HCl(g)} \qquad [B-3]$$

Again, comparing with the generalized eq. 11 we obtain:

$$c=1,\ d=1,\ e=1,\ f=2$$

Also, we have $M_C=154.92$, $M_E=100.01$, $M_F=36.46$, $\rho_C^\circ=1.92 g/cm^3$. CrO_3 is soluble in H_2O, however it is assumed that it does not have time to dissolve significantly since the time scale is on the order of only 10-20 s. In any event, the assumption of insolubility is believed not to introduce much error and is justified for the purposes of working this example. Therefore, we write:

$$x_E = 1.0,\ V_E = V_E^\circ,\ \rho_E = \rho_E^\circ = 2.70\ g/cm^3 \qquad [B-4]$$

Inserting the above values into eqs. 14 and 15, we obtain:

$$\frac{V}{V_C^\circ} = .45906 + \frac{0.90373}{\rho_F\, x_F} \qquad [B-5]$$

$$\frac{V_F}{V_E^\circ} = \frac{1.9686}{x_F\, \rho_F} \qquad [B-6]$$

The procedure now is similar to that done for the $VOCl_3$ calculations. The relationships between ρ_F and x_F and those between x_F and the relative humidity are obtained, for a given temperature, from Appendix A. The results are plotted in Figs. 2 and 3. See Figs. 6 and 7 for these ratios for CrO_2Cl_2 smoke at various temperatures.

APPENDIX C

Dissemination Techniques

C.1 The Mortar Technique

This method was first used by Tatyrek (see Ref. 8) and was adapted by both Levesque et al. and Wall (see Refs. 1, 9). It appears ideal for disseminating the liquid active agents and simulating the practice bomb bursts. The apparatus is identical to that used by Wall (see Ref. 9) and his diagram is reprinted here as Fig. C1. The apparatus has proved cheap, reliable, and effective.

C.2 High-Explosive Dissemination

This method calls for a charge of high explosive (C4 in this case) for dissemination but it was used only with iodine (I_2) by this author. With this procedure, a polyethylene jar is filled with the C4 explosive and the smoke agent. Polyethylene wrap is used to separate the C4 from the smoke agent (I_2). A hole is drilled in the cap through which the detonator wires may be passed.

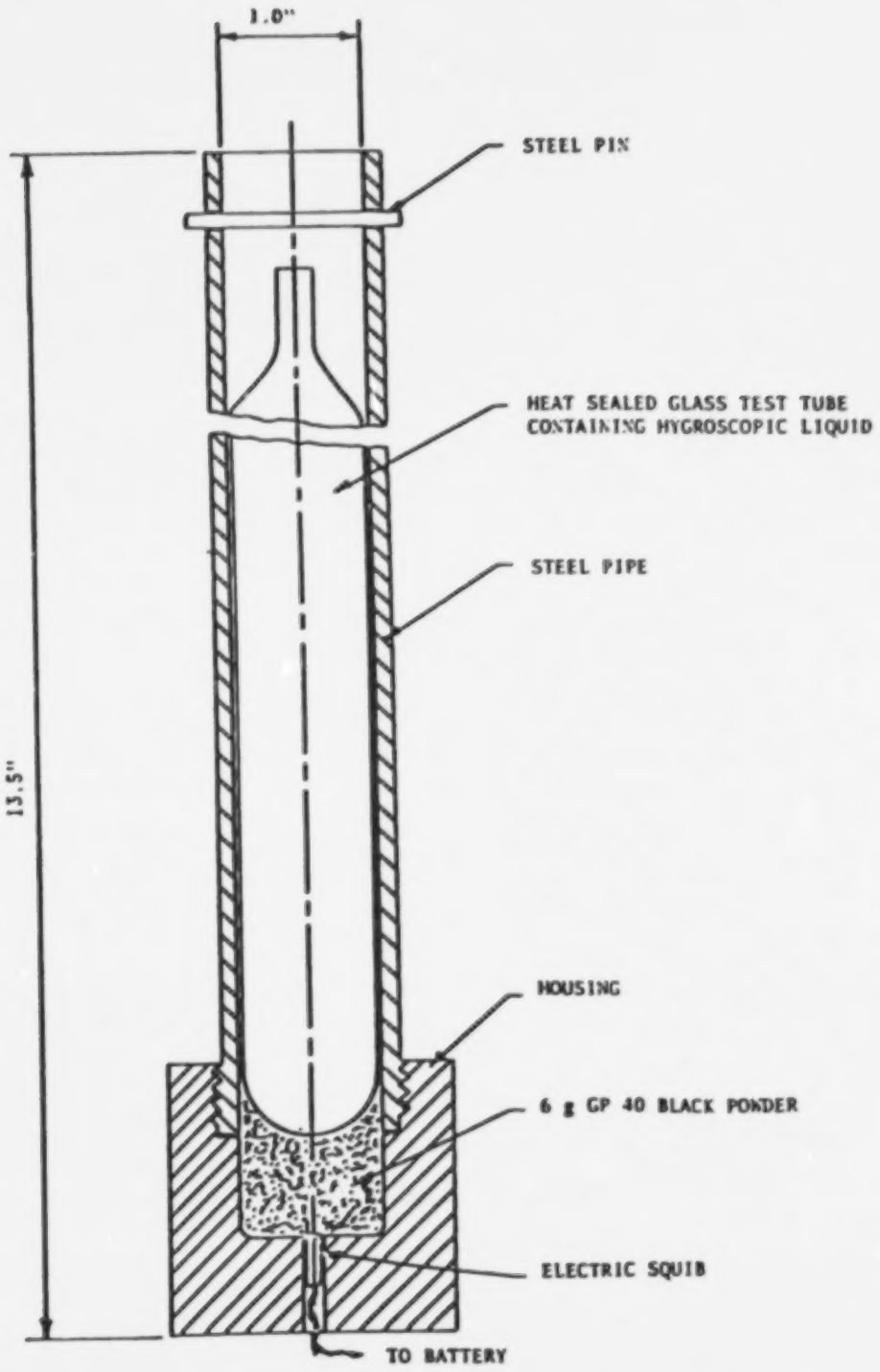

FIGURE C1 - Apparatus used to expel hygroscopic charges into the atmosphere

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"Investigation of Cold Colored Smoke Production" by T. Liberman

Different methods for producing large colored smoke clouds for use as spotting charges are evaluated. The problem of the disappearance, or "bleaching", of the orange color from vanadium oxytrichloride ($VOCl_3$) clouds during times of high relative humidity is considered. It is postulated that this is caused by the absorption of large quantities of atmospheric moisture by the smoke. A model has been developed to study the process. This model makes the key predictions concerning the absorption of very large amounts of atmospheric moisture by $VOCl_3$-type smokes above a relative humidity of 80% and the very small importance of temperature as a parameter. These predictions are, in general, corroborated very well by experiment. Possible solutions to this color bleaching problem are discussed, including one that calls for the synthesis of hydrolyzable vanadium compounds with nonhygroscopic leaving groups.

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"Investigation of Cold Colored Smoke Production" by T. Liberman

Different methods for producing large colored smoke clouds for use as spotting charges are evaluated. The problem of the disappearance, or "bleaching", of the orange color from vanadium oxytrichloride ($VOCl_3$) clouds during times of high relative humidity is considered. It is postulated that this is caused by the absorption of large quantities of atmospheric moisture by the smoke. A model has been developed to study the process. This model makes the key predictions concerning the absorption of very large amounts of atmospheric moisture by $VOCl_3$-type smokes above a relative humidity of 80% and the very small importance of temperature as a parameter. These predictions are, in general, corroborated very well by experiment. Possible solutions to this color bleaching problem are discussed, including one that calls for the synthesis of hydrolyzable vanadium compounds with nonhygroscopic leaving groups.

CRDV R-4372/85 (SANS CLASSIFICATION)

Bureau - Recherche et Développement, MDN, Canada.
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"Étude de la production des fumées colorées sans chaleur" par
T. Liberman

On a évalué différentes méthodes pour produire un large volume de fumée de couleur qui est utilisé comme repère. On traite du problème de décoloration de la fumée orange produite par l'oxytrichlorure de vanadium ($VOCl_3$) dans des conditions d'humidité de l'air ambiant qui pourraient en être la cause. Un modèle expérimental a été développé dans le but d'étudier le processus. Ce modèle prédit qu'une grande quantité d'humidité atmosphérique est absorbée par la fumée de type $VOCl_3$ lorsque l'humidité relative est au-dessus de 80% et considère la température comme un paramètre peu important. Les observations expérimentales corroborent généralement ces prédictions. Des solutions possibles au problème de décoloration sont discutées dont une qui fait appel à la synthèse des composés de vanadium hydrolysés avec des groupes non hygroscopiques.

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